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27. Rate of Hydrolysis[1] of Naphthalenemonosulfonic Acids

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We measured the rate of hydrolysis of naphthalene monosulfonic acids with hydrochloric acid in various concentrations in the temperature range from 140 to 180°C. The hydrolysis of sulfonic acids follows the first order rate law. Below 160°C, there is a linear relationship between the logarithm of the rate constants and the concentration of hydrochloric acid. At higher temperatures, the yield of hydrolysis reaches a maximum after a lapse of 1 to 1.5 hrs., and then it decreases owing to the resulfonation by the sulfuric acid produced, as reported by Lantz[2] in the hydrolysis of sulfonic acids with sulfuric acid. The temperature coefficient of the reaction was found to be 2.8 to 3.5, as shown in the following table.

Temp.	% HCl conc.	% hydrolysis in					k unimol. hr^{-1}
		1 hr.	2 hrs.	4 hrs.	6 hrs.	8 hrs.	
140°C	24.8	—	—	49.8	75.2	80.8	0.20
	22.0	—	14.1	34.3	52.9	—	0.10
	16.0	—	—	7.9	—	25.9	0.03
160°C	24.8	66.9	74.2	72.8	—	—	1.11
	22.0	43.7	71.8	80.7	92.8	—	0.60
	16.0	20.9	50.0	64.8	73.2	74.2	0.30
180°C	24.8	73.2*	82.8	—	—	—	2.64
	22.0	77.0*	89.8	86.8	—	—	2.61
	16.0	76.9	94.5	85.0	—	—	1.46

* one-half hour.

The β-sulfonic acid, which was used as Na-salt, is not hyldrolysed with 24.8 % HCl at 140°C, during 6 hrs., and even at 180°C, only 2.6 % of it could be hydrolysed with 22.0 % HCl. This results correspond to 1/250 of the rate of α-sulfonic acid. This difference between the rate of hydrolysis of α- and β-sulfonic acid can be utilized for analysing the mixture of α- and β-sulfonic acid. For this purpose it is recommended to treat the mixture with 16.0 % HCl at 180°C for 1 to 1.5 hrs.. The accuracy of this method is at maximum ±5.0 % in the content of α-sulfonic acid.

1) Crafts : Ber. **34** 1356 (1901)
2) Lantz : Bull. soc. chim. (5) **2** 2092 (1935)